ISSN 0704-3716

Canadian Translation of Fisheries and Aquatic Sciences

No. 5545

Anionic and non-ionic ethoxylate surfactants content in marine aerosol

L. Cleri, S. De Fulvio, P. Morgia, and A. Gaglio

Original title: Il contenuto di tensioattivi anionici e non ionici etossilati nell'aerosol marino

In: Riv. Ital. Sostanze Grasse/[Ital. J. Fatty Subst.] 67(June): 289-295, 1990

Original language: Italian

Available from:
Canada Institute for Scientific and Technical Information
National Research Council
Ottawa, Ontario, Canada K1A 0S2

1991

15 typescript pages

Secretary of State / Secrétariat d'État

MULTILINGUAL SERVICES DIVISION – DIVISION DES SERVICES MULTILINGUES

TRANSLATION BUREAU / BUREAU DES TRADUCTIONS

92-00819/

LIBRARY IDENTIFICATION – FICHE SIGNALÉTIQUE

Translated from - Traduction de	Into - En
Italian	English

Author - Auteur

L. Olori, S. De Fulvio, P. Morgia and A. Gaglio

Title in English or French - Titre anglais ou français

Anionic and non-ionic ethoxylate surfactants content in marine aerosol

Title in foreign language (Transliterate foreign characters)
Titre en langue étrangère (Transcrire en caractères romains)

Il contenuto di tensioattivi anionici e non ionici etossilati nell'aerosol marino

Reference in foreign language (Name of book or publication) in full, transliterate foreign characters.
Référence en langue étrangère (Nom du livre ou publication), au complet, transcrire en caractères romains.

La Rivista Italiana delle Sostanze Grasse

Reference in English or French - Référence en anglais ou français

Italian Journal of Fatty Substances

Publisher - Éditeur	DATE OF PUBLICATION / DATE DE PUBLICATION			Page Numbers in original / Numéros des pages dans l'original
	Year / Année	Volume	Issue No. / Numéro	299-295
Place of Publication / Lieu de publication	1990	LXVII	June	Number of typed pages / Nombre de pages dactylographiées: 15

Requesting Department / Ministère-Client: Fisheries and Oceans

Branch or Division / Direction ou Division: Dr. V. Zitko, Biological Station

Person requesting / Demandé par: St. Andrews, New Brunswick EOG 2X0

Your Number / Votre dossier nº: E-300

Date of Request / Date de la demande: 24 July 1991

Translation Bureau No. / Notre dossier nº: 3850550

Translator (Initials) / Traducteur (Initiales): RAY/LS

Canada

SEC 5-111 (84-10)

Department of the Secretary of State of Canada | Secrétariat d'État du Canada

TRANSLATION LETTERHEAD - PAPIER À EN-TÊTE

MULTILINGUAL TRANSLATION DIRECTORATE
TRANSLATION BUREAU

DIRECTION DE LA TRADUCTION MULTILINGUE
BUREAU DE LA TRADUCTION

Originator File No. - Référence du demandeur	Department - Ministère	Division/Branch - Division/Direction	City - Ville
	DFO	Scientific Pubs/Commun.	Ottawa, ON
Translation Request No. - N° de la demande de traduction	**Language - Langue**	**Translator (Initials) - Traducteur (Initiales)**	
3850550	Italian	RAY/LS	91/08/30

ANIONIC AND NON-IONIC ETHOXYLATE SURFACTANTS CONTENT IN MARINE AEROSOL*

L. Olori, S. De Fulvio, P. Morgia
Istituto Superiore di Sanità, Laboratorio Igiene Ambientale
[Higher Institute of Health, Environmental Hygiene Laboratory], Rome

and

A. Gaglio
III Clinica Chirurgica, IV Patologia Chirurgica
[Third Surgical Clinic, Fourth Surgical Pathology], University of Rome

Abstract

The anionic and non-ionic ethoxylate surfactant content in sea spray was studied using an analytical technique developed by the authors. A possible diffusion mechanism was investigated in addition to the relative contribution of surfactants in sea spray to acid rain. Finally, we calculated the correlation between rainfall and surfactant content in rainwater and sea spray.

INTRODUCTION

A series of accidents at industrial plants, in addition to the occurrence of toxins in commercial products have given rise to a growing public awareness of environmental protection and safety, resulting in ever tougher legislation and standards enacted by the Italian government. Clearly, our socioeconomic system has undergone a transformation and it is inconceivable that the terms of the ecological debate will remain unaffected.

The need to respect nature has evolved into a social movement that has not concentrated on either economic issues or opposing the system, but rather has focused on requiring that the environment be given equal consideration like any other factor of production.

---

*Paper presented at the Third CID Symposium at Sirmione, 20-21 October 1988.

SEC 5 - 1'3 88 4/1

Today a product that is technically feasible and economically viable, but environmentally unacceptable, is considered just as absurd as a product that respects the environment while making no economic sense.

Another problem today is humanity's blithe day-after-day undermining of our planet's quantitative and qualitative capacity to withstand the endless, pressing and growing demands made on it by our species.

We are fully aware that we cannot live without nature, from which we derive and on which we depend. Nonetheless, we continue unperturbed to destroy the "capital" that allows us to live, not knowing the intricacies of how living systems function, how the various chemical elements and their compounds interact, and what role soil, air, and water components play in the structure and proper functioning of the biosphere as a whole.

Of the multiplicity of chemical elements present in the universe, only five -- carbon, hydrogen, oxygen, sulphur, and phosphorus -- account for 95% of the total mass of matter on the globe. Phosphorus, which is contained in detergents, is believed to be primarily responsible for the eutrophication of bodies of water; however, this does not take into account that when balanced and controlled, its presence in complex biogeochemical cycles is of cardinal importance to life on our planet.

Here and abroad, a widespread concern for the environment is focusing on various economic aspects: process changes, product substitution (such as the present trend toward replacing polyphosphates in the formulation of detergents containing NTA, zeolites, citrates), the development of an anti-pollution industry, the creation of new professional specializations, and research in the environmental field. The latter is the aspect of applied research that concerns us most and that had led us to examine the area of detergents more thoroughly to evaluate the true causes and effects that the continuous, unchecked spread of surface-active agents might have on water ecosystems.

EXPERIMENTAL PART

The anionic and non-ionic ethoxylate surfactant content in sea spray was determined using an analytical technique developed by the authors (1). The anionic surfactant content of rainwater was also measured in order to ascertain a possible correlation between the surfactant content of the spray, the surfactant content of rainwater, and the acidification of water.

The study was carried out in an area overlooking the sea (San Rossore, Pisa), and in an adjacent pine forest. Five sampling stations were set up as shown in Figure 1. The sampling period (total 27 days) spanned the months of March to December 1983 and January 1984. The findings of the study are shown in Tables I and II and in the graphs in Figures 2, 3, 4, 5, 6, and 7.

Rainfall events refer to measurements taken on March 1, 1983, during drizzle with moderate offshore winds; from March 15 to 17, 1983, during rain with rather strong land winds; and from March 24 to 29, during heavy rains accompanied by strong onshore winds (*libeccio* or winds from the southwest).

The results of analytical studies show that during the period of maximum rainfall and strong onshore winds, non-ionic surfactant content was high, but there was no increase in the values for anionic surfactants.

Another noteworthy observation is the correlation between anionic surfactants in rainwater and aerosol as a function of rainfall. With drizzle, the surfactant content in rainwater was moderate at less than 1 mg/L, but concentrations increased with continuous rain or heavy rainfall (Figure 8, Table III) until they reached a state of equilibrium for an average rainfall of approximately 7 mm/day.

TABLE I. Non-ionic ethoxylate surfactants: average 24-hour concentration in $\mu g/m^3$ BIAS

Data = Date Postazione n. = Site no. Assente = None

Data	Postazione n. 1	Postazione n. 2	Postazione n. 3	Postazione n. 4	Postazione n. 5
12.3.1983	12,0	10,0	22,0	14,0	73,0
13.3.1983	110,8	109,9	142,8	114,0	149,2
14.3.1983	1621,0	231,0	189,0	499,0	165,0
15.3.1983	387,1	35,4	382,1	assente	assente
16.3.1983	231,0	409,0	744,0	425,0	357,0
17.3.1983	assente	150,0	733,0	461,0	170,0
18.3.1983	assente	assente	assente	assente	assente
19.3.1983	27,0	20,0	70,0	—	assente
20.3.1983	53,0	34,0	63,0	assente	68,0
21.3.1983	—	21,0	20,0	62,0	72,0
22.3.1983	8,0	8,0	134,0	43,0	15,0
23.3.1983	307,0	558,0	53,0	234,0	388,0
24.3.1983	185,0	810,0	493,0	231,0	250,0
25.3.1983	630,0	1212,0	572,0	47,0	155,0
26.3.1983	330,0	assente	531,0	14,0	78,0
27.3.1983	3,1	assente	86,3	assente	65,1
28.3.1983	46,9	assente	assente	52,3	49,9
29.3.1983	462,0	34,2	59,6	63,9	3,1
30.3.1983	114,5	477,4	65,5	39,9	3,5
6.12.1983	6,3	—	—	54,0	—
7.12.1983	5,8	—	—	17,4	—
8.12.83	5,4	—	—	17,2	—
9.12.1983	1,9	—	—	40,0	—
10.12.1983	217,4	—	—	750,0	—

TABLE II. Anionic surfactants: average 24-hour concentration in $\mu g/m^3$ (OT aerosol)

Data = Date Postazione n. = Site no. Assente = None

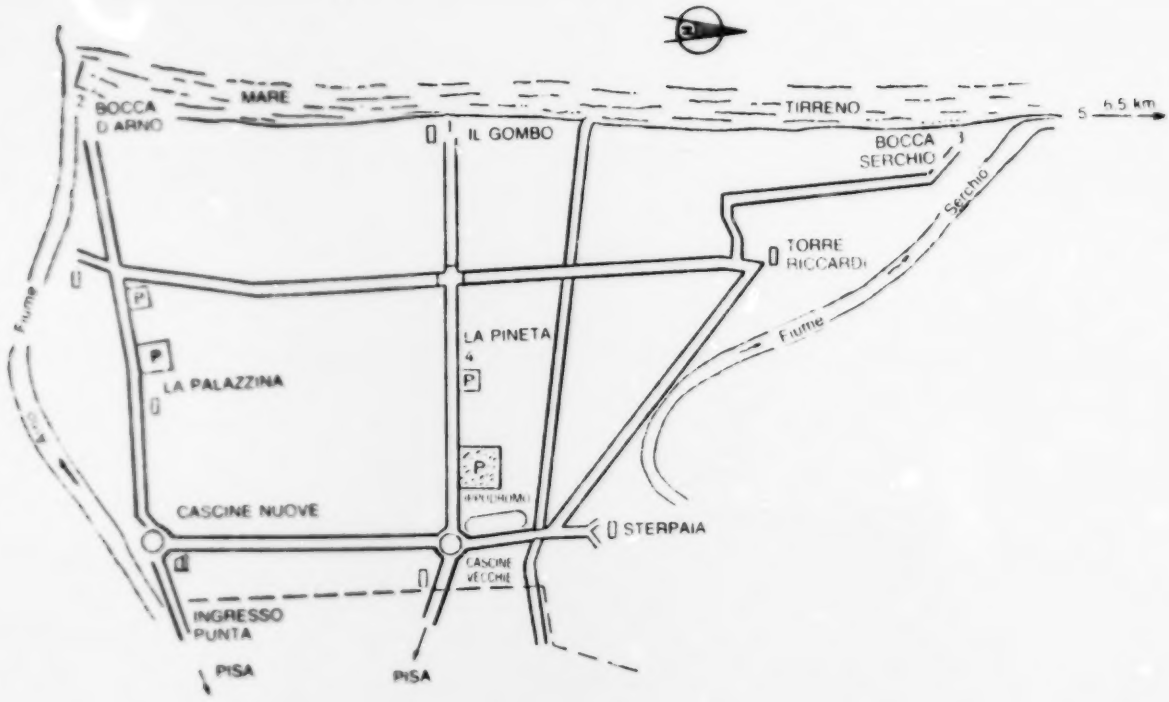
Data	Postazione n. 1	Postazione n. 2	Postazione n. 3	Postazione n. 4	Postazione n. 5
12.3.1983	3,0	4,0	4,0	5,0	2,0
13.3.1983	5,0	4,0	5,2	2,5	4,2
14.3.1983	7,0	1,0	3,0	2,0	1,0
15.3.1983	1,0	1,9	10,3	1,3	1,0
16.3.1983	1,0	4,0	1,0	1,0	1,0
17.3.1983	1,0	3,0	assente	1,0	1,0
18.3.1983	1,0	1,0	1,0	1,0	1,0
19.3.1983	1,0	1,0	1,0	—	2,0
20.3.1983	1,0	1,0	assente	assente	assente
21.3.1983	—	3,0	2,0	2,0	2,0
22.3.1983	10,0	2,0	4,0	5,0	10,0
23.3.1983	12,0	10,0	4,0	16,0	4,0
24.3.1983	1,0	4,0	3,0	15,0	3,0
25.3.1983	1,0	1,4	2,0	1,0	1,8
26.3.1983	1,0	1,0	1,0	1,0	1,0
27.3.1983	1,2	1,5	1,0	1,0	1,0
28.3.1983	1,0	1,0	1,0	1,7	1,3
29.3.1983	1,8	1,0	assente	1,0	1,2
30.3.1983	1,0	1,0	1,0	1,8	1,0
6.12.1983	1,9	—	—	3,6	—
7.12.1983	1,4	—	—	2,9	—
8.12.1983	1,3	—	—	1,4	—
9.12.1983	1,4	—	—	3,1	—
10.12.1983	4,5	—	—	99,2	—

TABLE III. Patterns in anionic surfactant content in aerosol and rainwater, with corresponding distribution coefficients (K)

Data prelievo	Tens. anionici conc. media ($\mu g/m^3$) nell'aerosol	Tens. anionici conc. media (mg/l) acqua di pioggia	Piovosità media giornaliera (mm)	Piovosità tot. (mm)	K 10^{-6} aria/acqua	pH acqua pioggia Batt	pineta
1.3.83	3.6	0.3	2.2	2.2	12	4.09	3.85
15.3.83	1.1	0.6	5.9		2	4.45	4.45
16.3.83	1.6	0.6	5.9	17.8	3		
17.3.83	1.2	0.6	5.9		2		
24.3.83	5.2	1.65	7.6		3	6.06	4.06
25.3.83	1.44	1.65	7.6		1	6.06	4.06
26.3.83	1.0	1.65	7.6	45.6	1	6.06	4.06
27.3.83	1.1	1.65	7.6		1	6.06	4.06
28.3.83	1.2	1.65	7.6		1	6.06	4.06
29.3.83	1.0	1.65	7.6		1	6.06	4.06

Key:
1. **Date of measurement**
2. **Average anionic surfactant concentration ($\mu g/m^3$) in aerosol**
3. **Average anionic surfactant concentration ($\mu g/L$) in rainwater**
4. **Average daily rainfall (mm)**
5. **Total rainfall (mm)**
6. **K·10-6 air/water**
7. **Rainwater pH**
   Batt. **Pine grove**

Figure 1. Map of Measurement Sites



Key:

Bocca d'Arno	Mouth of the Arno
Bocca Serchio	Mouth of the Serchio
Cascine nuove	New farmhouses
Cascine vecchie	Old farmhouses
Fiume Arno	Arno River
Fiume Serchio	Serchio River
Ingresso Punta	Entry to point
Ippodromo	Race-track
La Palazzina	Apartment building
La Pineta	Pine grove
Mare Tirreno	Tyrrhenian Sea
P	Measurement site
Sterpaia	Scrubland
Torre Riccardi	Riccardi Tower

The behaviour of anionic surfactants in spray and rainwater follows different analytical patterns, almost suggesting that rain performs a "clean-up" function in the atmosphere. As confirmation of this, there is the low coefficient of air/water distribution, which tends toward unity (equilibrium) at high levels of rainfall, with a function that tends to be substantially different for the rainwater and spray components.

TRANSFER MECHANISM

If we reduced the sea to the scale of a map of the world, it would be no thicker than a sheet of paper. Generally speaking, this means that the most important specific feature of the sea is neither its depth nor its total volume, but its surface area, which represents the largest and most homogeneous environment on our entire planet. This area of 360 million km^2 receives 70% of the solar energy reaching the surface of the earth, most of the inflowing freshwater, part of the annual CO_2 and 0_2 production, an enormous amount of solid material in the form of extremely minute particles, and an unknown quantity of pollutants spread by man.

Studies on the characteristics of this surface area form the basis of our understanding of the mechanisms that alter its properties when matter or energy passes through it.

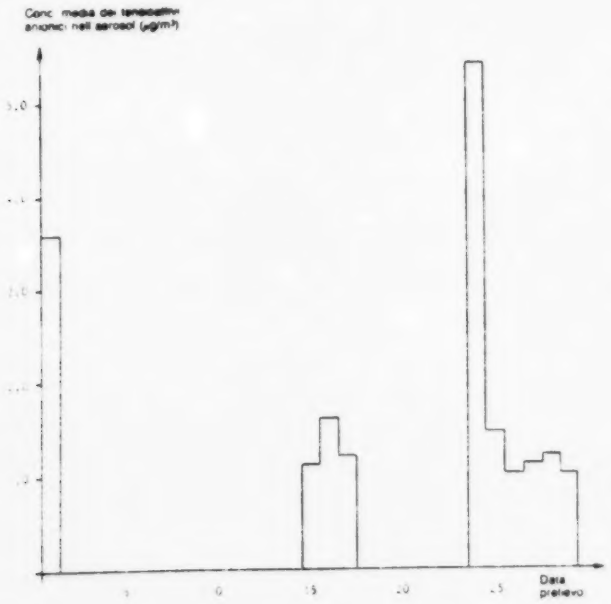
If we represent a section of the sea on a logarithmic scale, from the size of a water molecule (2 Å) to a maximum depth of 10 km (see Figure 9), we find that the uppermost millimetre of the sea (microlayer) accounts for the upper half of the total water mass.

Along this surface, a fractionation process takes place involving all the materials found in the microlayer. During fractionation, materials are released into the atmosphere (see Figure 10); some of these are chemically activated by solar energy, while others are catalytically activated by the atmospheric aerosol. The presence of surfactants on the level of several ppb may alter the surface properties of water, while at several ppm, it may alter the fractionation process drastically enough to mask the physicochemical mechanism of the transfer. In fact, any substance that increases the surface tension of the water tends to be repelled at the moment it spreads from the bottom to the top (J. Willard Gibbs), which explains the diffusion of surfactants in marine aerosol, the consequent formation of hydrochloric acid, and the acidification process in rainwater according to a mechanism of the following type:

$$R - CH_2 - (CH_2)_n - CH_2 - SO_3Na + H_2O \rightarrow$$
$$R - CH_2 - (CH_2)_n - CH_2 - SO_3H + NaOH$$
$$R - CH_2 - (CH_2)_n - CH_2 - SO_3H + NaCl \rightarrow$$
$$R - CH_2 - (CH_2)_n - CH_2 - SO_3Na + HCl$$

Figure 2. Average concentration of anionic surfactants in aerosol for five sampling sites.

Average concentration of
anionic surfactants
in aerosol ($\mu g/m^{3)}$



Sampling date

Key to Figures 3, 4, 5, 6, 7:

Title: Variation over time of non-ionic ethoxylate surfactant content at site 1 (Figure 3), site 2 (Figure 4), site 3 (Figure 5), site 4 (Figure 6), and site 5 (Figure 7).

Abscissa: Date of measurement

Ordinate: $\mu g/m^3$ BiAS in aerosol

Figure 3

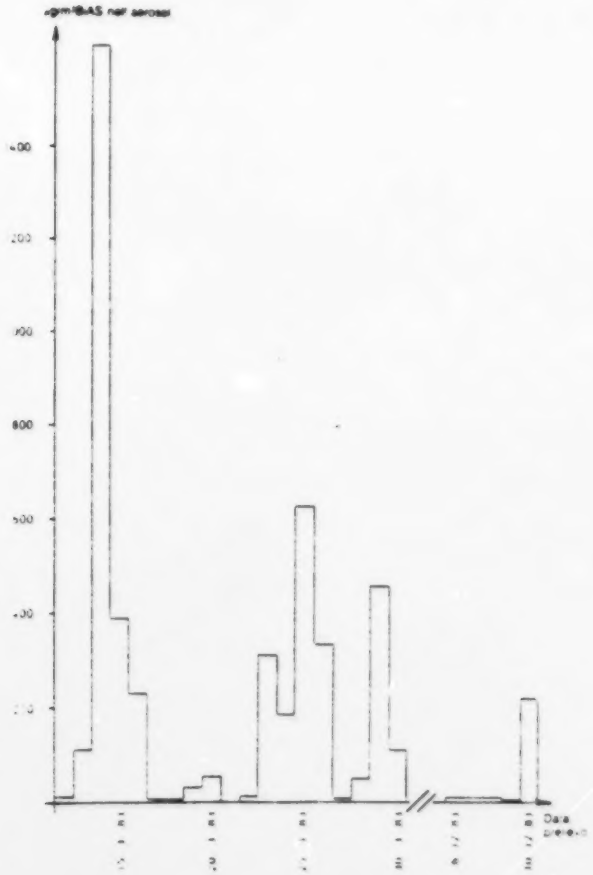


Figure 4

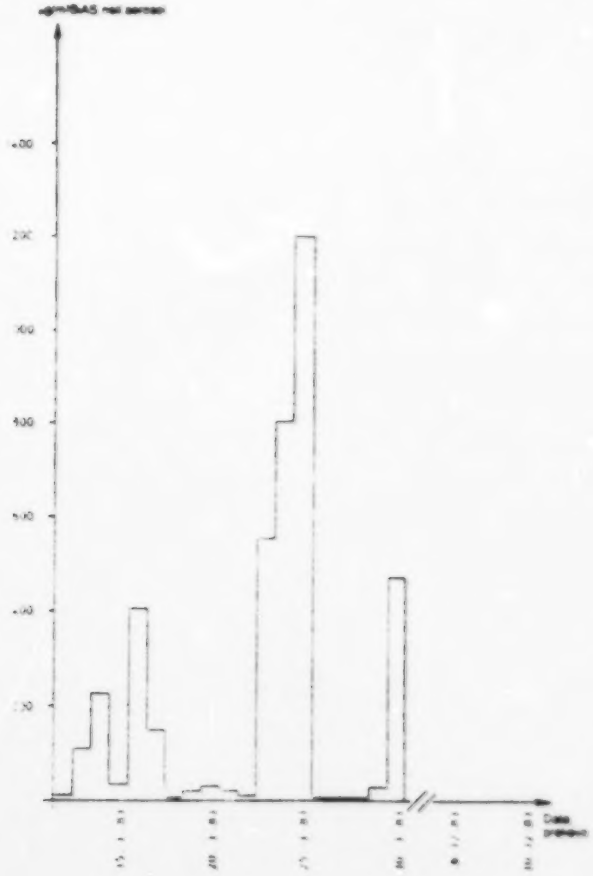


Figure 5

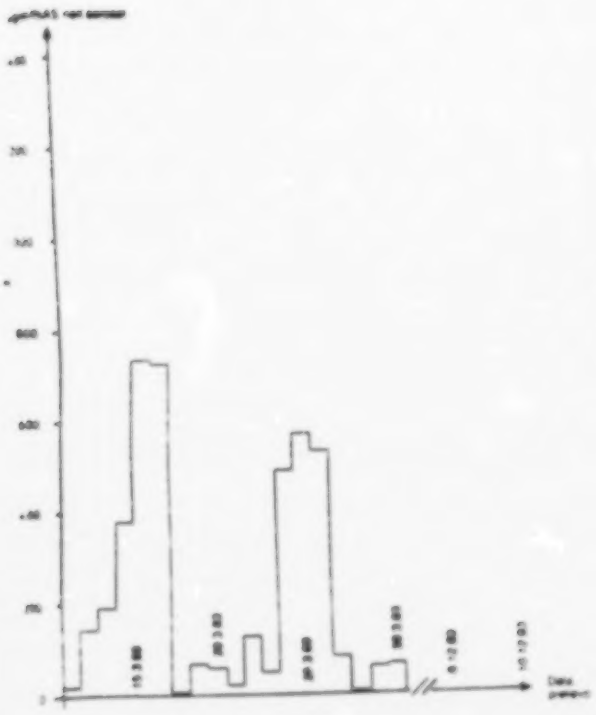


Figure 6

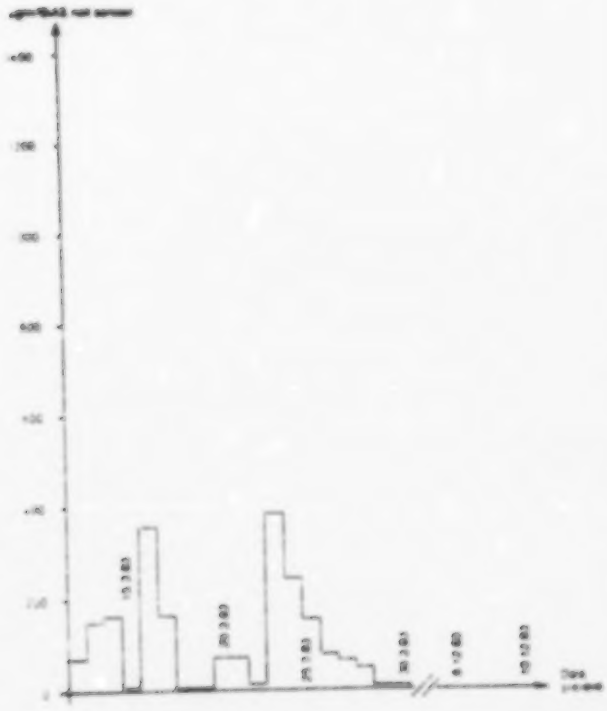


Figure 7

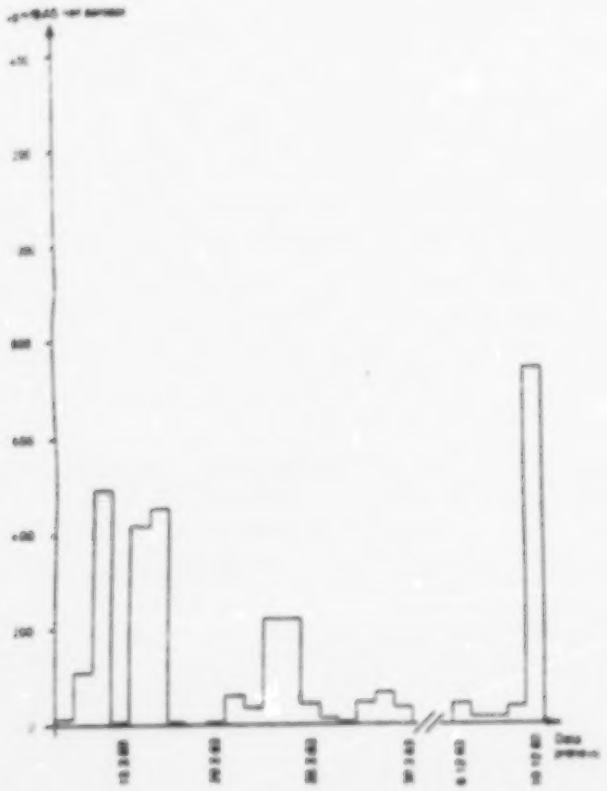
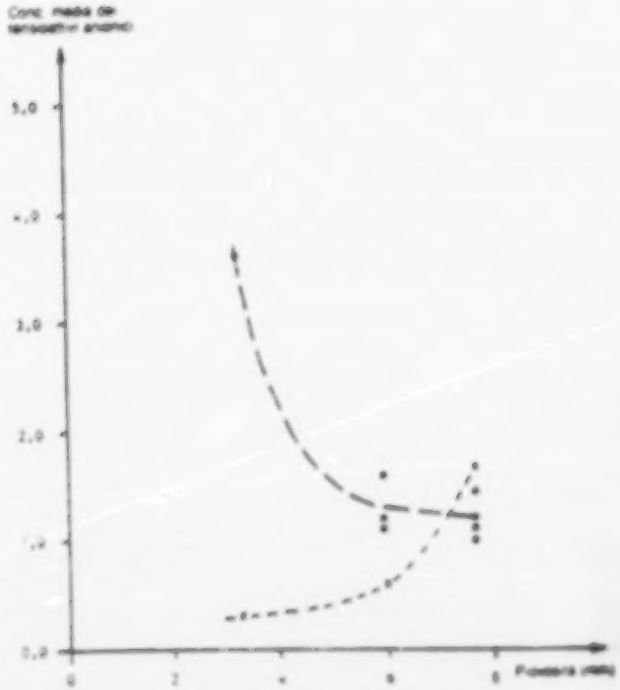


Figure 8. **Variation in anionic surfactant content in aerosol and rainwater with average rainfall**

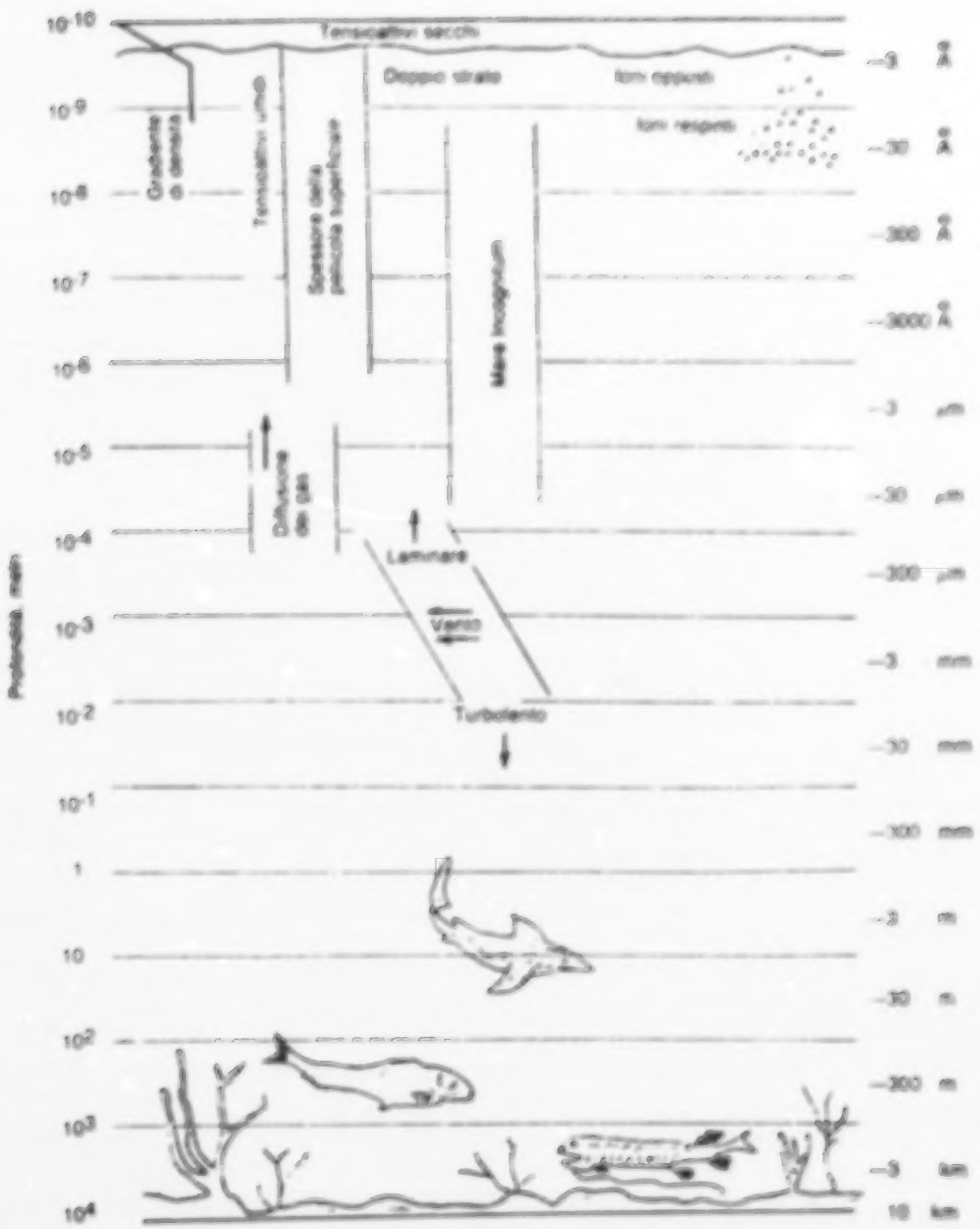
Average concentration of anionic surfactants

× = Rainwater (mg/L)
• = Aerosol ($\mu g/m^3$)



Rainfall (mm)

Figure 9

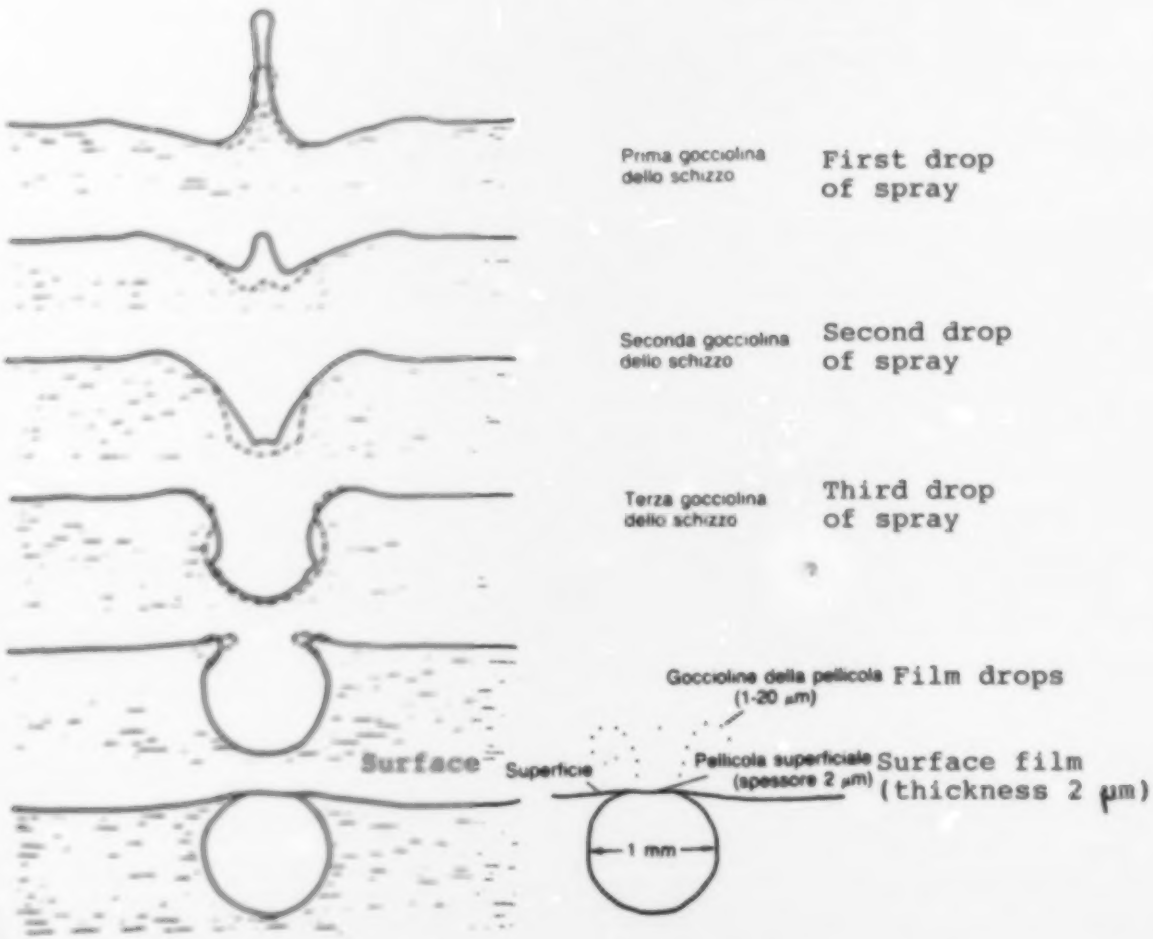


Key to Figure 9:

Diffusione dei gas	Gas diffusion	Profondità (metri)	Depth (m)
Doppio strato	Double layer	Spessore della pellicola superficiale	Thickness of surface film
Gradiente di densità	Density gradient		
Ioni opposti	Opposite ions	Tensioattivi umidi	Wet surfactants
Ioni respinti	Repelled ions	Tensioattivi secchi	Dry surfactants
Laminare	Laminar flow	Turbolento	Turbulence
Mare Incognitum	Mare Incognitum	Vento	Wind

Figure 10. Surfactant diffusion mechanism in aerosol by fractionation through the collapse of a bubble (according to Duncan C. Blanchard, A.H. Woodcock, et al.).

.....1/6000-second frame ----------1/3000-second frame



CONCLUSIONS

Our knowledge of the mechanisms of action and reactions of atmospheric aerosol remains insufficient for a complete understanding of the effects of its interaction with man-made compounds. It is difficult enough to distinguish the human component from natural fluctuations in climatic trends: the relationship between the recently discovered "hole" in the ozone layer over the Antarctic, for example, and the presence of freon and other pollutants in the upper atmospheric strata is still questionable. If we consider that air exchanges between the northern and southern hemispheres do not occur at the stratospheric level, it is not clear how the presence of pollutants concentrated in the industrialized northern hemisphere could have had an effect on the ozone layer at the South Pole, even though no such effect has yet been detected at the North Pole.

Nor has the correlation between acid rain and the crisis in Central European and North American forests been proven entirely, primarily because the use of coal, one of the major causes of acidification in these areas, was more prevalent in the past than today.

The acid rain problem might be of greater interest to us in the light of these additional studies and more detailed information, which could determine conclusively whether synthetic surface-active agents in sea spray are most directly responsible for acid rain.

As often happens, an appropriate scientific approach to environmental problems is undermined by certain groups within the "green movement", whose concerns are essentially groundless, naïve, and suggestive of anti-industrial nostalgia.

This state of affairs results in the failure to understand environmental problems and an acceptance of situations of "uncertainty" specific to our contemporary society. Nor do we believe it possible to deal with complex situations by framing them in simple right-or-wrong dichotomies, since anything can be right or wrong, depending on the circumstances.

A sense of direction is needed for the type of in-depth research required to provide constructive and authoritative development choices in Italy. In emergencies, the measures taken must be simplified, yet far-reaching, and based on the firm conviction that the environment must be seen as a holistic value; in other words, the environment must be viewed as a measure of all things, not, as is currently the case, as a pretext for pointing to problems without offering solutions.

• • • •

We wish to thank Professor Antonio Panebianco for his assistance in this research.

BIBLIOGRAPHY

1. L. Olori, F. Giorgi, "Determination of anionic and non-ionic ethoxylate surfactants in marine aerosols". World Surfactants Congress, Kurle Druck und Verlag Geinhausen, vol. III, pp. 324-330.

2. L. Olori, L. Cruciani, "Contaminanti in acque di pioggia ed impatto ambientale: prospettive per un indice di contaminazione" [Contaminants in rainwater and environmental impact: Outlook for a contamination index]. Atti convegno sulle attività di sorveglianza dell'inquinamento atmosferico in Italia [Proceedings of the convention on atmospheric pollution monitoring in Italy], Vigna di Valle, 27 September 1984.

3. M. Bondanini, L. Olori and U. Sannino, "Interazione uomo-ambiente: una realtà mutevole del clima" [Human-environmental interaction: the changing reality of climate]. Inquinamento [Pollution], January 1985.

4. Manuel international des pratiques de mesure de la pollution de fond, 1982, OMM, 491.

5. L.Olori, L. Lepore, U. Poli, R. Graziani, "Piogge acide: un confronto tra valori sperimentali di pH e di contenuto salino" [Acid rain: A comparison of experimental Ph values and saline content]. Ambiente e Sicurezza del Lavoro [Environment and occupational safety], No. 3, pp. 69-73 (1988).

6. Various authors, "Metodi analitici per le acque" [Methods of water analysis], vol. II, IRSA - CNR, 1983.

7. Apha, AWWA, WPCF, "Standard Methods for the Examination of Water and Wastewater", APHA N.Y., 1984.